

Claims:

1. A process for producing granular, particularly spherical activated carbon by carbonization of suitable carbonaceous polymers in the form of polymer granules, in particular polymer spherules, as a starting material, which are convertible by carbonization into carbon at least essentially,
5
characterized in
10 that the polymer granules, in particular the polymer spherules, are continuously moved through a carbonization apparatus comprising a plurality of temperature zones and/or a temperature gradient so that an at least essentially complete conversion of the starting material to carbon is effected.
- 15 2. The process according to claim 1, characterized in that the carbonization apparatus used is a continuous rotary tube or a continuous rotary tube oven, or else in that the carbonization apparatus used is a belt oven, in particular an oxidizing belt oven.
- 20 3. The process according to claim 1 or 2, characterized in that the polymer granules, in particular polymer spherules, are continuously moved through the temperature zones and/or the temperature gradient of the carbonization apparatus, in particular of the belt oven, by means of transporting or conveying means, in particular by means of a moving transporting or conveying belt, such that an at least essentially complete conversion of the starting
25 material to carbon is effected.
- 30 4. The process according to any one of the preceding claims, characterized in that the starting material used comprises polymers in the form of polymer granules, in particular polymer spherules, based on styrene and divinylbenzene and containing chemical groups which, when thermally decomposed, lead to free radicals and thus to cross-linkages, in particular strongly acidic groups such as sulfonic acid groups.

PCT/EP 2004/008314

5. The process according to claim 4, characterized in that the chemical groups leading to cross-linkages, in particular strongly acidic groups such as sulfonic acid groups, are already present in the starting material and/or in that the weight ratio of polymers to sulfonic acid groups is in the range from about 5:1 to about 1:1 and in particular in the range from about 2:1 to about 1:1.
6. The process according to claim 4 or claim 5, characterized in that the starting material used comprises ion-exchanger resins, in particular preferably strongly acidic cation exchanger resins, in particular ion-exchanger resins having sulfonic acid groups, and/or acidic organic catalysts, such as catalysts for bisphenol synthesis or for MTBE synthesis.
7. The process according to claim 6, characterized in that the starting material, in particular the ion-exchanger resins and/or the acidic organic catalysts, has added to it before and/or during the carbonization a sulfonating agent, preferably SO_3 , preferably in the form of sulfuric acid and/or oleum, in particular in an amount of about 1 % to about 30 % by weight of SO_3 , in particular 5 % by weight to about 25 % by weight of SO_3 , based on the dry weight of the starting material.
8. The process according to claim 4, characterized in that the chemical groups which, when thermally decomposed, lead to free radicals and thus to cross-linkages, in particular strongly acidic groups such as sulfonic acid groups, are, before and/or during the carbonization, introduced into the starting material, in particular by sulfonation, preferably by addition of a sulfonating agent, in particular SO_3 , preferably in the form of oleum and/or sulfuric acid, more preferably in the form of oleum mixed with sulfuric acid, in particular wherein the non-sulfonated polymeric starting material is before being introduced into the carbonization apparatus contacted with the sulfonating agent, preferably such that the polymeric starting material is at least essentially completely wetted with sulfonating agent.

PCT/EP 2004/008314

9. The process according to claim 8, characterized in that the sulfonating agent, in particular concentrated sulfuric acid and/or oleum, is used in relation to the polymeric starting material to be sulfonated in weight-based ratios of sulfonating agent/polymeric starting material in the range of from 0.2:1 to 2:1, in particular in the range of from 0.4:1 to 1.5:1, and/or in that the weight ratio of polymer/oleum 20 % is up to about 1:1 or more, and/or in that the weight ratio of polymer/oleum 20 %/sulfuric acid is about 1:1:0.5.
10. The process according to claim 8 or 9, characterized in that the starting material used comprises polymer granules, in particular polymer spherules, based on styrene and divinylbenzene, and/or in that the starting material used comprises precursors of ion exchanger resins.
11. The process according to one or more of the preceding claims, characterized in that the polymer granules, in particular polymer spherules, are porous, in particular macroporous, and/or gel-like.
12. The process according to any one of the preceding claims, characterized in that the carbonization apparatus comprises at least the following temperature zones in the following order:
- a) optionally, a first temperature zone ("sulfonating zone") where in the case that the starting material contains no groups which, when thermally decomposed, lead to free radicals and thus to cross-linkages, in particular no strongly acidic groups such as sulfonic acid groups, or else in the case that such groups are to be additionally introduced into the starting material, these groups are introduced into the starting material, in particular by sulfonation; then
 - b) a second temperature zone ("pre-carbonization zone" or "zone of acidic gases"), preferably having a higher average temperature than the first temperature zone, wherein in the second temperature zone the groups which, when thermally decomposed, lead to free radicals and thus to cross-linkages, in particular strongly acidic groups such as sulfonic acid groups, are detached or split off from the starting material, so that car-

PCT/EP 2004/008314

bonization and/or thermal decomposition of the starting material ensues, preferably accompanied by a crosslinking of the polymers and/or a formation of carbon; and then

5 c) a third temperature zone ("post-carbonization zone"), preferably having a higher average temperature than the second temperature zone, wherein in the third temperature zone further carbonization of the starting material resulting from the second temperature zone is performed, so that an at least essentially complete conversion of the start-
10 ing material to carbon is effected.

13. The process according to any one of the preceding claims, characterized in that the individual temperature zones are separately and/or independently controllable, and/or in that the individual temperature zones possess separate and/or independent exhaust means, so that the process gases from the
15 different temperature zones are separated and/or separately collected, and/or in that the carbonization apparatus comprises at least one lock, in particular between individual successive temperature zones and/or within individual temperature zones, preferably at least between the second and
20 third temperature zones, so that there is at least essentially no mixing through of process gases from different temperature zones between which at least one lock is disposed, and/or so that the acidic process gases from the second temperature zone are not mixed with the other process gases and can be collected separately, if appropriate followed by disposal or reproc-
25 essing with subsequent recycling.

14. The process according to any one of the preceding claims, characterized in that the process control is performed by setting the temperature profile in the individual temperature zones and/or the temperature profile of the tem-
30 perature gradient and/or by setting the speed at which the starting material moves through the temperature zones and/or the temperature gradient of the carbonization apparatus, and/or in that the total residence time of the start-
ing material in the carbonization apparatus is in the range from 0.1 to 5 hours, in particular in the range from 0.25 to 4 hours and preferably in the
35 range from 0.5 to 3 hours.

PCT/EP 2004/008314

15. The process according to any one of the preceding claims, characterized in that the first temperature zone is operated at temperatures in the range from 50 to 200 °C, in particular in the range from 75 to 175 °C and preferably in the range from 100 to 150 °C, and/or in that the second temperature zone is operated at temperatures in the range from 100 to 500 °C, in particular in the range from 150 to 450 °C, and/or in that the third temperature zone is operated at temperatures above 400 °C, in particular above 450 °C to 500 °C, and/or in that the third temperature zone is operated at temperatures in the range from 400 to 1.200 °C, in particular in the range from 450 to 1.000 °C, preferably in the range from 500 °C to 900 °C and more preferably in the range from 550 to 850 °C.
16. The process according to one or more of the preceding claims, characterized in that the carbonized material is subsequently subjected to an activation.
17. The process according to claim 16, characterized in that the activation is similarly carried out in the carbonization apparatus or else in that the activation is carried out in a distinct apparatus and/or at different locations and/or times than the carbonization.
18. The process according to claim 16 or 17, characterized in that the activation is carried out in a conventional manner, in particular wherein the activation is carried out in the presence of customary activating gases, such as oxygen, in particular in the form of air, water vapor and/or carbon dioxide or mixtures of these activating gases, preferably in the presence of a mixture of water vapor and nitrogen, and/or in particular wherein the activation is carried out at temperatures in the range from about 700 to 1.200 °C, in particular in the range from about 800 °C to about 1.100 °C, preferably in the range from about 850 °C to about 1.000 °C and more preferably in the range from about 900 to about 975 °C, and/or in particular wherein the duration of the activation is in the range from about 0.5 to about 20 hours, in particular in the range from about 2 hours to about 15 hours and preferably in the range from about 5 hours to about 10 hours.

PCT/EP 2004/008314

19. Activated carbon granules, in particular activated carbon spherules, obtainable by the process according to one or more of claims 1 to 18.
- 5 20. The activated carbon granules according to claim 19, characterized by an internal surface area in the range from about 800 m²/g to about 1.500 m²/g and preferably in the range from about 900 m²/g to about 1.200 m²/g, and/or by an average diameter in the range from about 0.1 mm to about 2.0 mm and preferably in the range from about 0.2 mm to about 0.8 mm with average values in the range from about 0.4 mm to about 0.6 mm,
10 and/or by a bursting pressure in the range from about 5 Newtons to about 20 Newtons per granule or spherule and/or by a riddled weight in the range from about 400 to about 800 g/l and preferably in the range from about 500 to about 750 g/l.
- 15 21. Use of activated carbon granules, in particular activated carbon spherules obtainable by the process according to one or more of claims 1 to 18 for producing adsorption materials such as adsorption (sheet) filters, filter mats, odor filters, sheet filters for protective suits, in particular for the civilian and/or military sector, filters for indoor air cleaning, gas mask filters
20 and adsorption-capable supporting structures.
22. Use of activated carbon granules, in particular activated carbon spherules, obtainable by the process according to one or more of claims 1 to 18 for protective materials, in particular protective suits against chemical poisons
25 such as warfare agents, or for filters, in particular filters for removing noxiant, poisonous and/or odoriferous entities from air or gas streams.
23. Adsorption materials, in particular filters of any kind such as adsorption (sheet) filters, odor filters, sheet filters for protective suits, in particular for
30 the civilian and/or military sector, such as protective suits against chemical poisons such as warfare agents, filters for indoor air cleaning and also protective suits produced therefrom, gas mask filters, filters for removing noxiant, poisonous and/or odoriferous entities from air or gas streams, filter mats and adsorption-capable supporting structures comprising activated
35 carbon granules, in particular activated carbon spherules, obtainable by the process according to one or more of claims 1 to 18.